

## INTRINSIC VISCOSITY OF LIGNITE-DERIVED PREASPHALTENES AND MODEL COMPOUNDS

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### INTRODUCTION

Non-covalent intermolecular interactions of coal-derived liquids have been studied by several researchers, particularly with respect to their effect on physical properties such as solubility and viscosity (1). Hydrogen bonding has been implicated in a number of studies as the principal attractive force responsible for the relatively high viscosity of coal asphaltenes (A) and preasphaltenes (PA) at ambient temperatures (2-10). For example, Bockrath and coworkers have reported that the viscosity of asphaltene solutions is predominantly a function of the phenol content (representing hydrogen bonding) and secondarily a function of molecular weight (representing van der Waals interactions) (4). Likewise, Tewari, et al., from studies of coal liquids (5,6) and model compounds (6) have demonstrated the importance of hydrogen bonding, largely involving phenolic OH and nitrogen bases, to the viscosity of coal liquids. Additional evidence for the importance of hydrogen bonding has been provided by derivatization studies. Gould and coworkers reported four- to seven-fold decreases in the viscosity of silylated coal liquefaction bottoms relative to the non-derivatized bottoms (9). Patel, et al. found a substantial increase in the dissolvability of solvent-refined lignite in nonpolar solvents after silylation or acetylation (10). The results of both investigations were interpreted in terms of disruption of intermolecular hydrogen bonding. Preasphaltenes have a greater impact on viscosity than do asphaltenes (3,7,9), but whether this is attributable to the larger molecular weight of the former (7) or to differences in concentrations of phenolic functionalities is not clear.

In connection with studies of intermolecular attractive forces in coal-derived liquids (12,13), we have measured the intrinsic viscosities of more than 60 model compounds and 6 lignite-derived preasphaltenes in THF solution. The goal of this project was to use well defined model compounds to assess the importance of various structural features, including molecular weight, functionality, and degree of aromatic condensation, to the intrinsic viscosity of the preasphaltenes.

### EXPERIMENTAL

Total liquefaction samples were obtained from the University of North Dakota Energy Research Center. Details regarding the liquefaction conditions and yields and characterization of the preasphaltenes are given in Table 1. A modified version of the solvent extraction procedure of Steffgen, et al. (14) was used to separate the preasphaltenes (THF soluble, toluene insoluble) from the total liquefaction samples. Room temperature acetylations of preasphaltenes from runs 80 and 99 were accomplished following the method of Baltisberger, et al. (15). Both native and acetylated preasphaltene samples were separated into narrow molecular size fractions by preparative gel permeation chromatography (GPC) on Biobeads S-X3 or S-X8. Model compounds employed were either commercially available or were prepared by standard literature methods.

Specific viscosities of the preasphaltene samples and model compounds were measured in THF solution at 20 °C in Canon-Fenske flow-type viscosimeters. Intrinsic viscosities were calculated by extrapolation of plots of specific viscosities/concentration vs. concentration to infinite dilution. Viscosity and molecular weight data for selected model compounds and separated preasphaltene samples are presented in Table 2.

## RESULTS AND DISCUSSION

Intrinsic viscosities were determined for THF solutions of lignite-derived preasphaltenes samples from six different liquefaction runs (Table 1). The values obtained are quite similar, despite differences in processing conditions. The two samples with the highest intrinsic viscosities were those with the lowest carbon content and the highest oxygen content. One may be tempted to interpret these results in terms of the influence of polar oxygen functionalities in the preasphaltenes. However, GPC analysis of the preasphaltene samples revealed that the highest average molecular weights were exhibited by those same two samples. Thus, one may also suggest that the slight differences observed in the measured intrinsic viscosities may be ascribed to differences in molecular weight, and hence, nonspecific interactions such as van der Waals forces. Recent work by White and Schmidt has revealed the existence of a linear relationship between the average molar polarizability of Wilsonville and H-Coal liquefaction product distillates (boiling points from 400-900°F) and the mid-boiling point of those same distillates (16). Since the mid-boiling point is representative of the total intermolecular forces and polarizability is directly related to van der Waals forces, the authors concluded that the dominant intermolecular force in these distillates was van der Waals forces.

Because of the complexity of the preasphaltene samples, model compounds were employed to address the question of the relative importance of specific interactions such as hydrogen bonding and charge-transfer versus nonspecific interactions such as van der Waals forces to the intrinsic viscosity of the samples. The model compounds were chosen to evaluate four principal structural features: degree of aromatic condensation (representative of charge-transfer), aromatic carbon content (charge-transfer), hydrogen bonding functionalities, and molecular weight (representing the nonspecific interactions). Table 2 contains the intrinsic viscosity data for approximately half of the model compounds used in the study. The influence of aromatic condensation can clearly be seen by comparison of naphthalene with tetralin or decalin, phenanthrene with bibenzyl and perylene with 1,1'-binaphthyl. For each pair, the molecular weights are comparable, yet the more highly condensed aromatic compound possesses a greater intrinsic viscosity. Likewise, the aromatic carbon content influences the intrinsic viscosity. Compare, for example, tetraethylpyrene with perylene. The former is 62 g/mole heavier than the latter, but has a smaller intrinsic viscosity. This is likely due to the ethyl groups of tetraethylpyrene sterically interfering with stacking interactions of the aromatic nuclei. Both the degree of condensation and the aromatic carbon content apparently contribute to the intrinsic viscosity via charge-transfer interactions of the aromatic rings. The importance of hydrogen bonding functionalities to intrinsic viscosity is more pronounced than either of the two previous structural features. As expected, NH species exhibit a decreased effect in comparison to OH species (cf. 1,2,3,4-tetrahydroquinoline vs. tetralin with 2-naphthol vs. naphthalene). An increase in the number of hydrogen bond donating groups leads to a concomitant increase in intrinsic viscosity that is much larger than could be expected on the basis of an increase in molecular weight alone (cf. 2,7-naphthalenediol with 2-naphthol). The influence of molecular weight is perhaps best noted by comparisons of polystyrene oligomers. These samples differ in molecular weight without differing in aromatic condensation or aromatic carbon content (weight percent). Thus the observed differences in intrinsic viscosity may be attributed solely to differences in molecular weight and hence, nonspecific forces.

Assessment of the relative importance of specific vs. nonspecific forces is difficult and clouded by the fact that in most cases, an increase in the degree of condensation, aromatic carbon content, or number of hydrogen bonding moieties is accompanied by an increase in molecular weight. A potential approach to this dilemma is to use the Mark-Houwink equation ( $[\eta] = KM^a$ ), which polymer chemists employ to relate molecular weight to intrinsic viscosity. Plots of the logarithmic form of this equation for the model compounds are presented in Figure 1A. The slopes of the least-squares lines for each data set correspond to the value of  $a$  in the Mark-Houwink equation. Model compounds which differ primarily in molecular weight alone yield a significantly smaller  $a$  value than model compounds which differ in

molecular weight and possess the capability of some specific interaction, either hydrogen bonding or charge transfer. Thus, one would suggest that contributions arising from specific forces outweigh those from nonspecific forces.

An analogous argument may be applied to the preasphaltene samples. Separation of two total preasphaltene samples into narrow molecular weight fractions was accomplished by preparative GPC. A logarithmic Mark-Houwink plot of the preasphaltene data is given in Figure 1B. For both the native and acetylated samples of PA-80, the value of  $a$  is closer to that obtained from the model compounds which exhibit specific interactions. On the other hand, the  $a$ -values for the samples of PA-99 are similar to that of the nonspecific interaction model compounds. Therefore, the individual preasphaltene samples do not appear to be uniform in the structural features which play a crucial role in determining intrinsic viscosity. As in many cases involving coal liquids, generalization regarding intrinsic viscosity may not be appropriate.

Comparison of molar volumes of the model compounds and separated preasphaltenes calculated from intrinsic viscosity with molar volumes calculated from density affords a semi-quantitative measure of the interaction of the solute with the solvent (THF). These data are reported in Table 2 as  $n_{THF}$ . Hydrogen bonding with the solvent is clearly identifiable for low molecular weight model compounds with phenolic functionalities (cf. naphthalene, 2-naphthol, 2,7-dihydroxynaphthalene). Other functional groups (OR, NH) also cause association beyond that expected on the basis of size alone. Functional group contributions to THF association may be determined from these data to be 1.0 THF molecule per OH, 0.4 THF/OR and 0.2 THF/NH. Without question, however, as the molecular weight increases, the dominant contributing factor to THF association is molecular size. This can readily be seen for both the model compounds and the preasphaltene samples in Figure 2.

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TABLE 1. Coal liquefaction conditions and preasphaltene (PA) characterization.<sup>a</sup>

Run no.	Temp. (°C)	Press. (MPa)	Additive	Yield PA <sup>b</sup>	Analysis <sup>c</sup>					Intrinsic viscosity
					C	H	N	S	Od	
80	456	22	H <sub>2</sub> S	10.7	77.8	6.1	2.1	0.7	13.3	3.90
89	436	19	H <sub>2</sub> S	9.0	81.6	5.6	2.6	0.6	9.6	3.78
90	436	15	-	11.2	83.8	5.4	2.3	0.3	8.2	3.63
93	440	15	S	8.6	81.9	5.5	2.5	0.6	9.5	3.57
98	440	14	H <sub>2</sub> S + pyrite	6.2	81.2	5.7	2.6	0.6	9.9	3.52
99	400	16	-	19.6	80.1	5.7	2.1	0.4	11.7	3.99

<sup>a</sup>All runs were carried out with Big Brown Texas lignite under bottoms recycle operation with H<sub>2</sub>-CO as the reducing gases

<sup>b</sup>Yields are based on starting weight of total coal liquefaction product

<sup>c</sup>Weight percent

<sup>d</sup>By difference

Table 2. Intrinsic viscosities and THF association of selected model compounds and separated preasphaltene samples.

Compound	MW	$[\eta]^a$	$n_{THF}^b$
Benzene	78	0.24	0.1
Naphthalene	128	1.43	1.0
Biphenyl	154	1.54	1.3
Phenanthrene	178	1.94	1.9
Chrysene	228	2.34	2.9
1,1'-Binaphthyl	254	2.30	3.2
Perylene	252	2.64	3.7
Diphenylmethane	168	1.40	1.3
Fluorene	166	1.64	1.5
Bibenzyl	182	1.58	1.6
1-Methylnaphthalene	142	1.22	1.0
2,6-Dimethylnaphthalene	156	1.30	1.1
Tetralin	132	1.15	0.9
Decalin	138	1.02	0.8
1,3,6,8-Tetraethylpyrene	314	1.93	3.5
1-(2-Naphthalenylmethyl)pyrene)	342	2.91	5.4
Carbazole	167	2.13	2.0
Quinoline	129	1.51	1.1
5,6,7,8-Tetrahydroquinoline	133	1.20	0.9
1,2,3,4-Tetrahydroquinoline	133	1.81	1.3
2-Naphthol	144	2.58	2.0
2,7-Naphthalenediol	160	4.11	3.6
2-Methoxynaphthalene	158	1.60	1.4
2-Naphthol acetate	186	1.61	1.7
2,7-Naphthalenediol diacetate	244	2.11	2.8
4,4'-Biphenol	186	4.22	4.3
4,4'-Biphenol diacetate	270	2.35	3.4
1-Pyrenol	218	2.88	3.5
Pentaphenyl ether	446	2.77	6.8
Polystyrene	615	2.68	9.3
Polystyrene	1140	3.45	22.4
Polystyrene	2500	4.90	69.0
Poly(2-vinylnaphthalene)	570	3.24	9.8
Poly(2-vinylnaphthalene)	1150	3.96	25.1
PA-80-1N	1202	7.53	50.0
PA-80-2N	470	2.90	8.0
PA-80-3N	375	1.85	4.7
PA-80-4N	272	1.88	3.1
PA-80-1A	1077	5.31	32.4
PA-80-2A	605	2.58	9.3
PA-80-3A	520	2.38	7.7
PA-80-4A	313	1.55	3.2
PA-99-1N	1382	5.32	40.0
PA-99-2N	584	4.13	13.1
PA-99-3N	443	3.77	9.3
PA-99-4N	337	3.58	6.8
PA-99-1A	1080	4.35	28.2
PA-99-2A	614	3.46	11.8
PA-99-3A	478	2.93	7.7
PA-99-4A	370	2.82	5.6

<sup>a</sup>Intrinsic viscosity

<sup>b</sup>Number of THF molecules associated with one molecule of compound

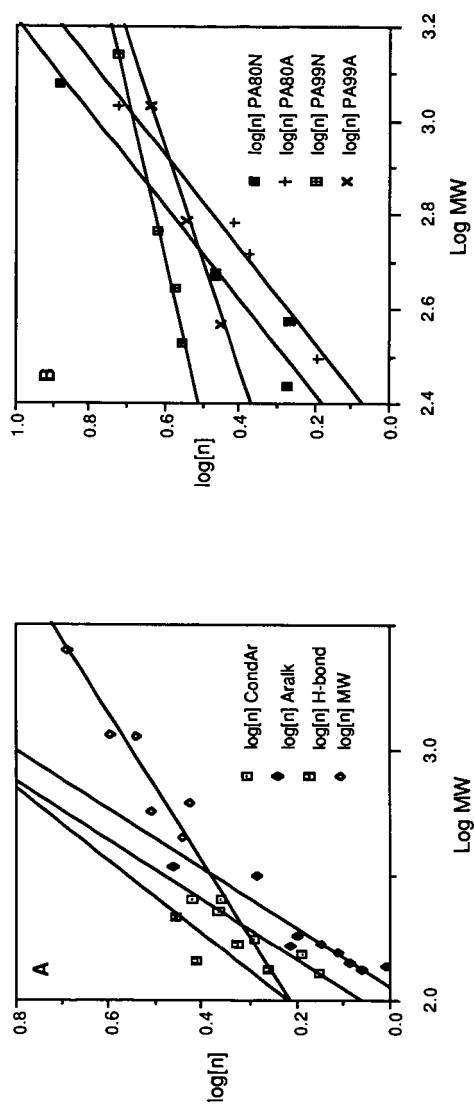


Figure 1. Plots of log intrinsic viscosity ( $[\eta]$ ) vs. log molecular weight for selected model compounds and separated preasphaltenes. (A) CondAr = condensed aromatic models, Aralk = alkyl- and hydroaromatic models, H-bond = model compounds with one functional group capable of hydrogen bonding with THF, MW = polystyrene and poly(2-vinylnaphthalene models. (B) N = native (nondervitized), A = acetylated.

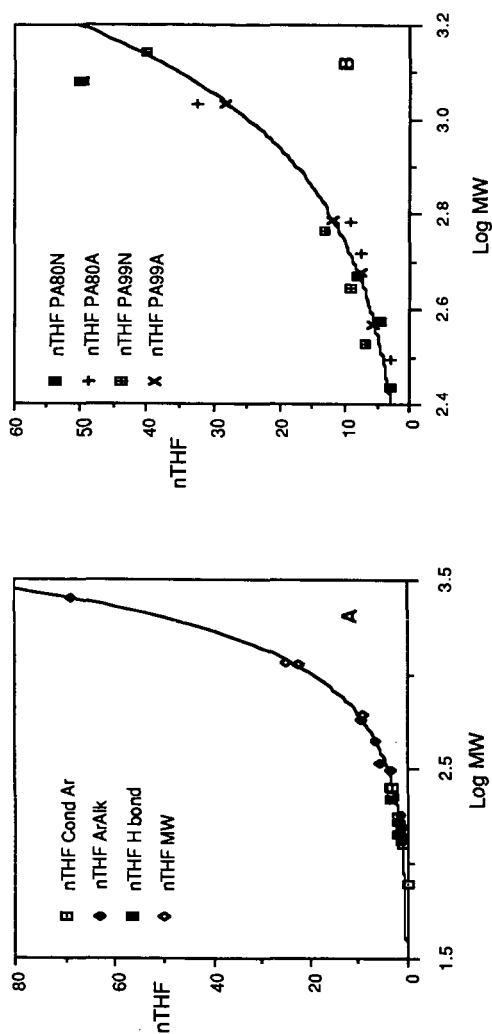


Figure 2. Plots of number of THF molecules associated with selected model compounds and separated preasphaltenes (nTHF) vs. log molecular weight. Symbols and abbreviations are the same as for Figure 1.